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Direct Observation of Non-strain-free Style Domain in $BaTiO_3$ Crystal by Synchrotron X-ray Topography

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We performed X-ray diffraction topography on a $BaTiO_3$ single crystal by high-coherent synchrotron X-rays. Since the domain configuration of the $BaTiO_3$ crystal was unstable and fluctuated as temperature fluctuated, an excellent temperature control system is needed for the domain observation. We used a milli-Kelvin (mK) cell, which can control a $BaTiO_3$ crystal within ±1mK. By combining the coherent X-ray and the mK-cell, one can detect the lattice strain very sensitively around the domain boundary. The lattice strain reduced as temperature increased, and disappeared at 100°C, which is much lower than the phase transition temperature of the $BaTiO_3$, and the $BaTiO_3$ crystal still remained in the ferroelectric tetragonal phase. This behavior can be interpreted by the existence of the so-called "non-strain-free style domain", which is reported firstly by Takashige *et al.*
Key words: $BaTiO_3$, synchrotron X-ray, topography, domain observation

1. INTRODUCTION

Since the discovery of ferroelectricity in $BaTiO_3$ in 1945, it has been one of the most exhaustively studied materials [1]. At high temperatures, it has the classic ABO_3 (with Ba^{2+} as A and Ti^{4+} as B) perovskite structure. This is a centrosymmetric cubic structure with A at the corners, B at the center, and oxygens at the face centers. However, as the temerature is lowered, it goes through successive phase transitions to three different ferroelectric phases, each involving small distortions from the cubic symmetry. At 393 K, it undergoes a paraelectric to ferroelectric transition to a tetragonal structure, it is orthorhombic between 278 and 183 K and, finally, it is rhombohedral below 183K. Each of these distortions can be thought of as elongations of the cubic unit cell along an edge ([001] or tetragonal), along a face diagonal ([011] or orthorhombic), or along a body diagonal ([111] or rhombohedral). These distortions result in a net displacement of the cations with respect to the oxygen octahedra along these directions. It is primarily these displacements that give rise to the spontaneous polarization in the ferroelectric phases. Earlier theory suggested that the structural instabilities arise from the small Ti^{4+} ion "rattling" around in the octahedral oxygen cage [2]; however, this is difficult to reconcile with the TiO bond lengths which do not differ much from the sum of the Ti^{4+} and O^{2-} ionic radii [3]. Instead, recent electronic structure calculations by Cohen [4] suggest that it is the competition between covalent and ionic forces involving Ti and O that leads to these instabilities. These instabilities bring the structural instability, which is observed as the polarization instability or the crystal coherency, and it may reconcile with domain configurations.

Kwei *et al.* noticed large changes in the average powder extinction depending on the temperature [5]. The changes in the extinction reflect changes in the mosaic structure of the crystallites. In the powder experiments, the structural instabilities reflect the mosaic block size. On the other hand, in the single crystal experiments, the structural instabilities reflect the crystal coherency. However, in my knowledge, there has been few observation of the change in the structural coherency in ferroelectric materials except Takashige's work [6]. Tahashige *et al.* performed the 90-degree domain (in the tetragonal phase) observation of a $BaTiO_3$ single crystal with atomic force microscopy (AFM). The 90-degree domain can be visualized by detecting the tilt angle between *a*-domain and *c*-domain. They reported that some domain boundaries suddenly disappeared at temperatures about 10°C lower than the Curie point. They introduced a new domain model, as shown in Fig.1, which is called "non-strain-free style domain". The tilt angle of the non-strain-free style domain was too small to detect by the AFM observation. This observation suggested that the coherent area of the ferroelectric domain was enlarged due to the absence of the surface tilting.

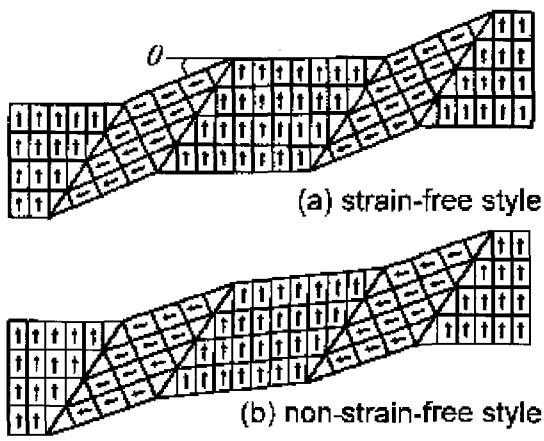

Fig. 1 Schematic illustrations of lattice matching at the 90° domain boundaries. (a) Strain-free crystal. Rectangles present tetragonal unit cells. Tetragonality is exaggerated. (b) Non-strain-free crystal. Note that this figure is drawn under the assumption that two *c*-domains on both sides are strain-free.

We have already performed synchrotron X-ray topography on a $BaTiO_3$ multi-domain crystal at the tetragonal phase. The synchrotron X-ray can be detected the lattice strain, which was generated at the ferroelectric domain boundary [7,8]. The polar direction of a *c*-domain was tilted slightly from the other *c*-domains due to the lattice strain from the domain boundary. By concerning Takashige's work and our previous work, the crystal coherency was changed by the domain configuration. However, our previous work did not clarify the reduction of the tilting angle of the non-strain-free style domain. In this paper, we performed the strain detection with the high-coherent synchrotron X-ray. The purpose of this article is the direct observation of the non-strain-free style domain.

2. EXPERIMENTAL SETUP

X-ray diffraction topography from a $BaTiO_3$ crystal was studied in an X-ray diffractometer scheme at the optics beamline BL47XU, an undulator beamline of SPring-8 (see Fig. 2). The undulator gap was 12 mm and 8 keV X-rays were used. X-ray energy was selected by a double Si (111) monochromator. Primary slit with vertical and horizontal gaps of 100 × 100 μm and ϕ = 20 μm pinhole slit were used to improve the X-ray coherency. The diffractometer can achieve an angular resolution of ~ 1 arcsec. An ionization chamber counter was used to measure the diffracted intensity. When the X-ray diffraction topography performed, the reflected beam image was recorded by a 2D X-ray detector (Beam Monitor, BM) with the pixel size of 40 μm. The BM consisted of a fluorescent screen and a CCD (C4742, Hamamatsu Photonics Co.).

3. SAMPLE

$BaTiO_3$ single crystal was grown by the top-seeded solution growth method, which was provided from MTI Co. in USA. The crystal was vergin sample in a sense

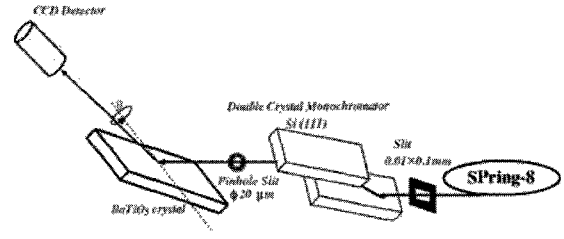

Fig. 2 Schematic diagram of experimental setup. ionization chamber was replaced with CCD camera when X-ray topography was performed.

with no external electric field applied prior to the measurements. It was cut in a cube with 5 mm with the thickness of 1.5 mm. The sample was supported in a small cupper cell of the milli-Kelvin (mK)-stabilized cell [9] and the sample temperature was controlled within ±1 mK.

4. EXPERIMENTAL RESULTS

4.1 Rocking curve measurement

Preliminary experiment of rocking curve measurement was performed by a laboratory X-ray system using Mo-K_α radiation monochromatized by a Si (111) crystal. The full width at half maximum (FWHM) of the rocking curve of the $BaTiO_3$ (002) reflection was 0.28°, as shown in Fig. 3. The crystal quality was good enough to perform the synchrotron X-ray measurements.

4.2 Strain from domain boundary

Figure 4(a) shows the optical microscope image of the $BaTiO_3$ sample. The stripe 90-degree domain configuration was observed at room temperature. The domain width was 20 - 40 μm, which was less than the beam size of the synchrotron X-ray. When the X-ray beam was hit at the center of the 90-degree domain [indicated by a white circle (b) of Fig. 4(a)], the reflected beam image of the (002) reflection was a small spot, as shown in Fig. 4(b). The small beam spot indicated that the crystal coherency was good at the center of the 90-degree domain. On the other hand, when the X-ray beam was hit at just the domain

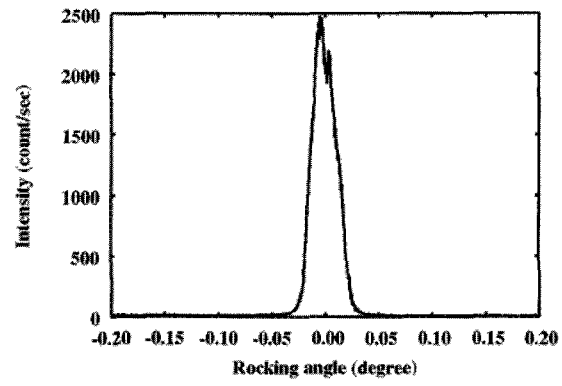

Fig. 3 Rocking curve measurement of the $BaTiO_3$ single crystal using laboratory X-ray system.

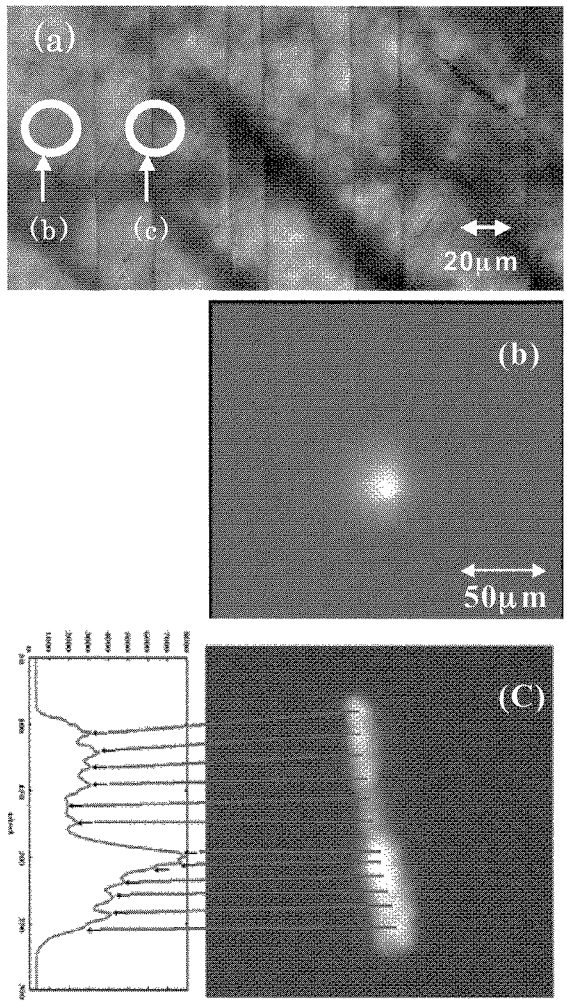

Fig. 4 (a) Optical microscope image of the $BaTiO_3$ single crystal. (b) CCD image of the X-ray reflected beam of (002) reflection from the center of domain. (c) CCD image of the X-ray reflected beam of (002) reflection from the domain boundary.

boundary [indicated by a white circle (c) of Fig. 4(a)], the reflected beam image of the (002) reflection was spread out, as shown in Fig 4(c). The reflected beam was separated depending on the crystal coherency and the diffraction image consisted of many reflected spots. The crystal coherency was reduced by the lattice strain from the domain boundary, and the lattice strain exists only around the domain boundary.

4.3 Temperature control

The sample temperature was controlled by the mK-stabilized cell specialized for the synchrotron X-ray measurement. Since the high-resolution and high-coherent synchrotron X-ray beam was used for this experiment, well-stabilized temperature control system is needed. If the temperature fluctuates, both lattice parameter and the domain configuration of the $BaTiO_3$ sample will also fluctuate. As a result, the Bragg reflection becomes dim and an accurate strain detection can not be performed. Figure 5(a) shows the CCD image

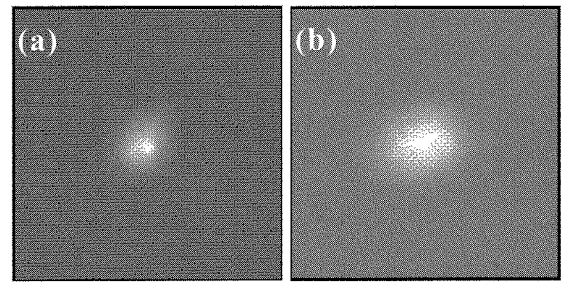

Fig. 5 CCD image of the X-ray reflected beam of (002) reflection at 125°C with the temperature fluctuation (a) ±1 mK and (b) ±1 K.

of the (002) reflection from the center of domain at the temperature of 125°C. When the temperature fluctuated ±1 mK, the small spot was observed, indicating the Bragg diffraction image from the static domain can be observed. On the other hand, when the temperature fluctuated ±1 K, the Bragg diffraction image became dim, as shown in Fig. 5(b). Therefore, we controlled the sample temperature ±1 mK during the synchrotron X-ray measurements to obtain the Bragg diffraction image from the static domain configuration.

4.4 Temperature dependence

The temperature dependence of the lattice strain from the domain boundary can be visualized by detecting the beam profile, as shown in Fig. 4 (a). When the crystal net plane is tilted due to the lattice strain, the reflected beam will be separated depending on the tilted net plane. On the other hand, when the X-ray was hit on the unstrained area, the sharp spot will be observed. The schematic diagram of strain detection mechanism is shown in Fig. 6.

Figure 7 shows the temperature dependence of the reflected beam profile from the $BaTiO_3$ (002) reflection. The incident X-ray beam hit the 90-degree domain boundary of the tetragonal phase. At the beginning of this experiment, the reflected beam was split as mentioned before. Although the separated peak became diffuse peak with increasing temperature, the beam profile remained to separate up to the temperature range from 40 to 80°C. When the temperature reached to 90°C, the separated peak of the diffuse part suddenly disappeared. Finally, the smaller spot was observed at

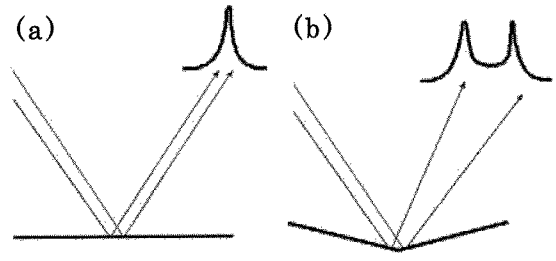

Fig. 6 Schematic diagram of strain detection mechanism by high-coherent synchrotron X-ray. (a) Reflected beam with untilted crystal net plane shows a singlet peak. (b) Diffracted beam is split depending on the tilted crystal net plane.

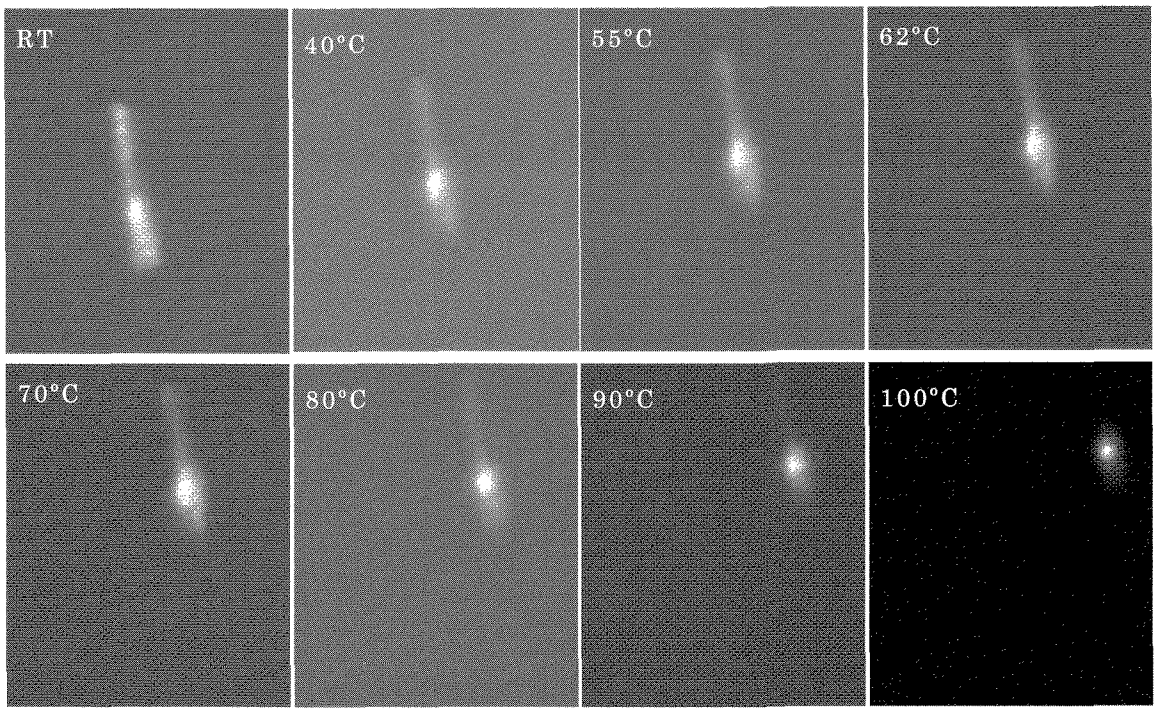

Fig. 7 Temeprature dependence of reflected beam profile of (002) reflection collected by CCD. The reflected beam was separated in twelve spots due to the tilting of the crystal net plane at room temperature. The tilting of the net plane suddenly disappeared at 90°C.

100°C, and it remained just before the tetragonal-cubic phase transition occurred. The transition temperature from the tetragonal to the cubic phase of this sample was 131.4°C. The lattice strain from the domain boundary was relaxed without phase transition and without changing the domain configuration. This is related to the strain relaxation effect. As a result, the coherency of the $BaTiO_3$ crystal improved. This strain relaxation is the direct evidence of the existence of the non-strain-free style domain.

5. SUMMARY

We observed the lattice strain of the $BaTiO_3$ single crystal from the domain boundary. The static domain configuration can be observed by the mK-stabilized temperature control system. The lattice strain disappeared around 90°C, that is much lower temperature than the Curie point. The lattice strain from the domain boundary was reduced and the crystal coherency improved by the formation of the non-strain-free style domain.

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